

UDC 666.124

USE OF A MECHANICALLY DISPERSED MIXTURE $\text{SiO}_2 + \text{Se}$ AS A COLORANT FOR OBTAINING TINTED GLASS

L. N. Bondareva,¹ I. N. Gorina,^{1,3} A. B. Zhimalov,¹ I. D. Kosobudskii,² and G. A. Polkan¹

Translated from *Steklo i Keramika*, No. 5, pp. 7–9, May, 2011.

A selenium-based colorant obtained by transferring it into micro- and nanostates by mechanical dispersion using the main component of the glass — quartz sand — as the stabilizing matrix is studied. It is determined that with mechanical dispersion of $\text{SiO}_2 + \text{Se}$ mixtures not only does comminution occur but a transition of selenium into other polymorphic modifications could also occur, while the observation of an increase of the color intensity of the glasses synthesized on their basis is most likely due to the stabilization of selenium particles in low-dimension voids of the quartz glass. It has been found that a black heterogeneous mixture $\text{SiO}_2 + \text{Se}$ is characterized by high volatility and simultaneously the highest tinting power.

Key words: tinted glass, colorants, selenium, heterogeneous mixture, mechanically dispersed, micro- and nanodispersed states.

There is great interest in the use of nanomaterials for technological purposes. It is known that because of the size effect nanoparticles can engender qualitative changes in the properties of the materials and articles made based on nanoparticles. However, aggregation and instability of the nanoparticles which results in the loss of a number of properties limit the applications of nanotechnologies. In this connection, studies of stabilization of nanoparticles in the solid phase, including on the surface and in the volume of the stabilizing matrix, have undergone extensive development [1–4].

The development of effective methods of preparing colorants for the production of tinted glass has been under study at the Saratov Institute of Glass, JSC (“SIS,” JSC) for a number of years [5–6].

The present article gives the results of investigations of a colorant based on selenium, obtained by transferring it into the micro- and nanodispersed state by means of mechanical mixing using as the stabilizing matrix the main component of the glass batch — quartz glass.

The mixtures $\text{SiO}_2 + \text{Se}$ were comminuted and activated using high-intensity grinders — the “Sand” centrifugal-planetary mill and the AGO-2S planetary, fractional, discrete, activator [4, 5]. The content of Se (colorant) in the mixture $\text{SiO}_2 + \text{Se}$ was varied from 2 to 15%.⁴

The intensity of the effect of a mechanical impulse on the material being comminuted was regulated by changing the operating parameters of the mill as well as the processing time of the mixtures. The samples of heterogeneous mixtures and glass samples obtained were investigated with differential thermal analysis, x-ray phase analysis, IR spectroscopy, and microscopic and visual examination; the degree of coloring of laboratory samples of the glasses was used to study how effectively the colorants are used technologically.

It is shown in [5–6] and the present studies confirm that for a mechanically dispersed mixture $\text{SiO}_2 + \text{Se}$ not only are the mixtures comminuted but the color of the mixture changes from red to gray and black, i.e., it is possible that a transition of selenium into other polymorphic modifications (Fig. 1), obtained, as a rule, by special methods, occurs [7].

Most samples of the mixtures $\text{SeO}_2 + \text{Se}$ show on their differential thermographic analysis curves a decrease of the volatility of selenium (to about 20%) depending on the degree of mechanical action [5, 6]. As x-ray phase and x-ray structural analyses showed, in most samples the dominant phase of the heterogeneous mechanically dispersed mixtures $\text{SiO}_2 + \text{Se}$ is the α -quartz phase of SiO_2 with $d = 4.350, 3.340, 2.455, 2.270, 2.227 \text{ \AA}$ and so on ASTM [21-462]. The Se reflections (hexagonal structure) at $d = 3.754, 2.988, 2.176, 2.064 \text{ \AA}$ and so on ASTM [6-362] are negligible and depend on the Se concentration in the mixture. Broadening of the diffraction lines and intensification of the background are observed in the samples, which attests to the structural imperfection of the quartz and the presence of an amorphous component.

¹ Saratov Institute of Glass, JSC, Saratov, Russia.

² Saratov State Technical University, Saratov, Russia.

³ E-mail: gorina@narat.ru.

⁴ Here and below — content by weight.

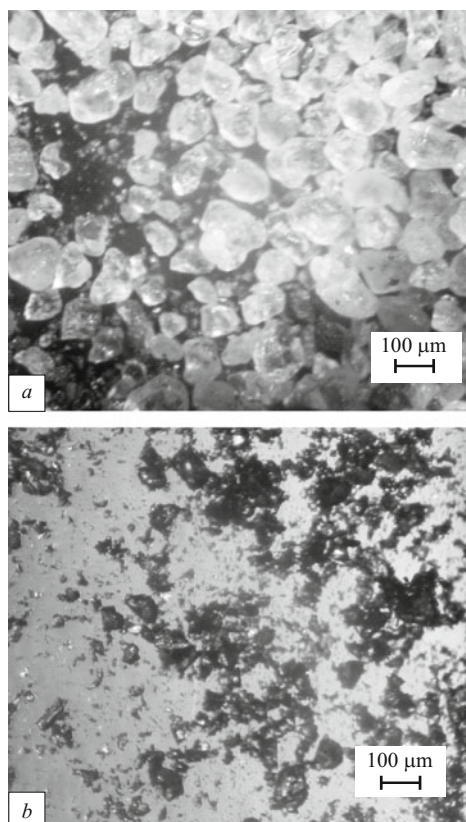


Fig. 1. Photomicrograph of the initial (a) and mechanically dispersed mixture (b) $\text{SiO}_2 + \text{Se}$.

Comparative glasses made in the laboratory at $t_{\text{max}} = 1420^\circ\text{C}$ with the molten glass soaked at the maximum temperature for 2.5 h showed that the lowest coloring power is seen for red, mechanically dispersed, heterogeneous mixture $\text{SiO}_2 + \text{Se}$ but depending on the processing regimes used for the mixture and the color change of the mixture to gray and lack the degree of coloring of the experimental samples of the glasses increases, probably as a result of the stabilization of the selenium particles in a low-dimensional voids of the quartz sand.

Results differing from all other series of samples were obtained in a study of black heterogeneous mixtures $\text{SiO}_2 + \text{Se}$.

A considerable decrease of the SiO_2 phase was recorded in the x-ray diffraction patterns of black heterogeneous mixtures $\text{SiO}_2 + \text{Se}$. At the same time a sharp rise of the volatility of the mixture with a maximum endo-effect at temperatures $640 - 700^\circ\text{C}$ is observed on the DTA and TG curves (Fig. 2). The degree to which the mass decreases (volatilizes) in individual samples is more than twice the amount of selenium introduced into the mixture, and in individual series a higher degree of mass change (volatilization) of the mixture was recorded.

The comparative results of glassmaking in laboratory electric furnaces and in a periodic gas-flame furnace (capacity 600 kg selenium) confirmed a substantial increase of the

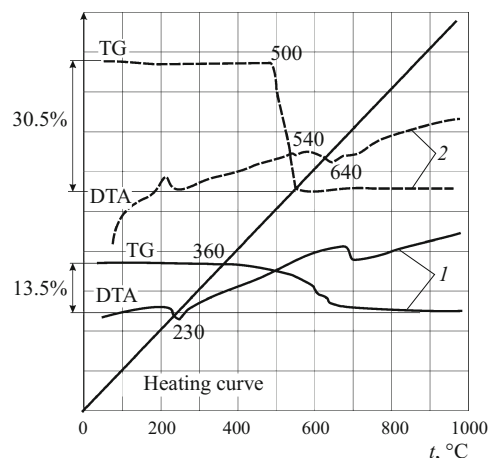


Fig. 2. DTA and TG curves of samples of the initial 1 and mechanically dispersed 2 heterogeneous mixture $\text{SiO}_2 + \text{Se}$ (15 wt.% Se).

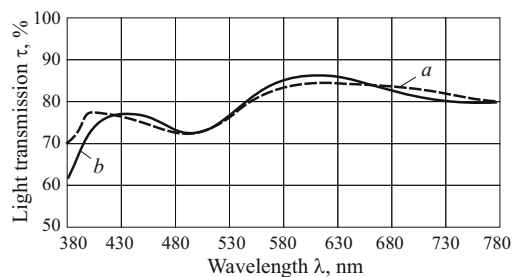


Fig. 3. Spectral curves of the experimental glass samples: a) based on metallic selenium; b) based on a mechanically dispersed black mixture $\text{SiO}_2 + \text{Se}$ (5 wt.% Se).

coloring power of the mechanically dispersed black mixture $\text{SiO}_2 + \text{Se}$.

Figure 3 shows spectrograms of the transmission of experimental glass samples synthesized by using as the colorant metallic selenium (a) and mechanically dispersed heterogeneous mixtures $\text{SiO}_2 + \text{Se}$ (5 wt.% Se) (b).

The synthesized glass samples into which the same amount of colorant was introduced (a) and (b) had the same color and their spectral curves were the same. The IR transmission spectra of these experimental glasses and “Rozalin” glass are identical [8]. Two wide absorption curves are observed in the all spectral curves in the visible region of the spectrum. The first and most intense band is characterized by an absorption maximum near 500 nm, and the second absorption band at $700 - 750 \text{ nm}$ has a diffuse absorption maximum. The intensity of the reflections on the spectral curve of the experimental sample (b) is close to that of the control sample (a), where metallic selenium was used as a colorant.

Studies of the indicated heterogeneous black mixtures $\text{SiO}_2 + \text{Se}$ using modern methods of analysis have been initiated at the “SIS” JSC. The local structure of the selenium environment in the metallic powder and in the mechanically dispersed black mixture $\text{SiO}_2 + \text{Se}$ with 5 wt.% Se was in-

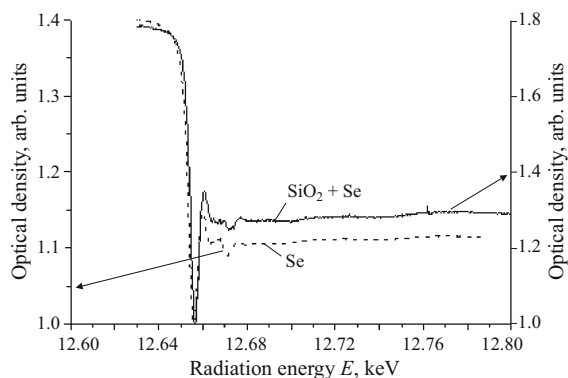


Fig. 4. EXAFS spectra of the samples of mechanically dispersed mixture $\text{SiO}_2 + \text{Se}$ and metallic Se.

vestigated by EXAFS. According to this method the radiation beam was monochromatized by a double silicon crystal monochromator with third-order filtering. Detection was performed with ionization chambers at room temperature. The spectra were processed and a nonlinear fit of the model was made using the standard program Viper. In making the fit the types of atoms surrounding selenium were taken into account to determine the most reliable model.⁵ The EXAFS spectra of the heterogeneous mixture $\text{SiO}_2 + \text{Se}$ and metallic selenium are presented in Fig. 4; the results of the nonlinear fit of the EXAFS spectra are presented in Table 1. Curves of the radial distribution of the atoms are presented in Fig. 5. It is evident that the degree of interaction of the selenium with its environment is stronger in the sample of the mixture $\text{SiO}_2 + \text{Se}$ than in metallic selenium. This can be judged by the change of the coordination number (see Table 1) and increase of the intensity of peak at the absorption edge of the selenium (see Fig. 4), while the total agreement of the coordination distances indicates that in both cases selenium is also most likely found in the environment around selenium (Table 1). The structure of this sample cannot be identified with any type of crystal lattice. There are known modifications of selenium with a cubic or hexagonal lattice, and information about its spiral local structure is also encountered in the literature [7].

⁵ We thank V. I. Kochubei, Doctor of Physical-Mathematical Sciences and Professor, for performing the measurements and analyzing the samples by the EXAFS method.

TABLE 1. Nonlinear Fit of the EXAFS Spectra

Sample type	Coordination No.	Coordination distance, Å	Degree of disorder
Metallic selenium	0.08603423	2.3662139	0.017318110
Mechanically dispersed mixture ($\text{SiO}_2 + \text{Se}$)*	2.10915200	2.3754990	0.004404301

* Se content 5 wt.%.

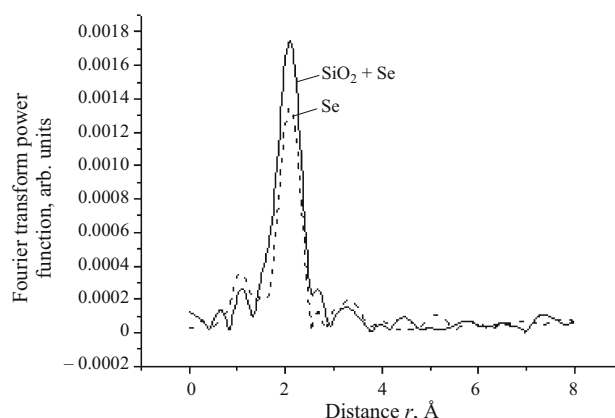


Fig. 5. Curves of the radial distribution of the atoms.

The radial distribution curves of the atoms (see Fig. 5) in the dispersed mixture $\text{SiO}_2 + \text{Se}$ and in metallic Se are very close.

In summary, the present studies have established that for mechanically dispersed heterogeneous mixtures $\text{SiO}_2 + \text{Se}$ not only comminution but also a transition of selenium into other polymorphic modifications possibly occurs, the degree of volatilization of the selenium decreases in most cases and the color intensity of the glasses synthesized based on them increases, which is most likely due to the stabilization of selenium particles in low-dimension voids of the quartz sand. In addition, it was found that heterogeneous black mixtures $\text{SiO}_2 + \text{Se}$ are characterized by enhanced volatility and simultaneously the highest coloring power.

REFERENCES

1. N. F. Uvarov and V. V. Boldyrev, "Size effects in the chemistry of heterogeneous systems," *Usp. Khim.*, **70**(4), 308 – 309 (2001).
2. A. Mueller and S. Royes, "Nano-objects based on metal oxides: reactivity, structural blocks for polymer structures, and structural diversity," *Usp. Khim.*, **71**(12), 1107 – 1118 (2002).
3. Yu. S. Avramov, N. P. Kalashnikov, V. I. Koshkin, et al., "Development of composite materials using intense physical impulses on the contact zone of solid metal substances," in: *Proc. 5th Russian–Japanese Seminar on Equipment, Technology, and Analytical Systems for Materials Science, and Micro- and Nano-Electronics* [in Russian], MISiS, Moscow (2007), Vol. 2, pp. 729 – 733.
4. I. D. Kosobudskii, V. V. Simakov, N. M. Ushakov, and G. Yu. Yurkov, *Physical Chemistry of Nano-Size Objects: Composite Materials* [in Russian], Izd. SGTU, Saratov (2009).
5. L. N. Bondareva, I. N. Gorina, A. B. Zhimalov, et al., "Development of effective methods of preparing colorants for the production of glasses colored in the bulk," in: *Stekloprogress–XXI: Scientific Reports*, Privolozhskoe izd., Saratov (2008), pp. 102 – 109.
6. L. N. Bondareva, I. N. Gorina, A. B. Zhimalov, et al., "Use of mechanically dispersed mixtures as colorants to obtain glasses colored in the bulk," in: *Stekloprogress–XXI: Scientific Reports* [in Russian], "KUBiK," JSC, Saratov (2010), pp. 166 – 170.
7. D. M. Chizhikov and V. P. Schastlivyi, *Selenium and Selenides* [in Russian], Nauka, Moscow (1964), pp. 7 – 22.
8. I. Kotsik, I. Nebrezhenskii, and I. Fanderlik, *Coloration of Glass* [in Russian], Stroiizdat, Moscow (1983), pp. 67 – 68.